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(54) Title: LIQUID CRYSTALLINE POLYMER-POLY(PHENYLENE OXIDE) BLENDS

(57) Abstract

Blends of thermotropic liquid crystalline polymers and unfunctionalized poly(phenylene oxides) in which the dispersed phase domain size is relatively small can be made by melt mixing the two types of polymers. These blends have good physical properties and can be used as molding resins.

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Title
LIQUID CRYSTALLINE POLYMER-POLY(PHENYLENE OXIDE) BLENDS

This application claims the benefit of U.S. Provisional Application No. 60/052,808, filed July 9, 1997.

Field of the Invention

Novel blends of liquid crystalline polymers and unfunctionalized poly(phenylene oxide) polymers in which the discontinuous phase has a relatively small average particle size, or co-continuous phases are present, are described.

Technical Background

Blends of various polymers are well known in the art, such blends often having advantages over unblended polymers such as improved physical properties and/or lowered cost. It is also known that to have good properties it is often desirable that the polymers in a blend be intimately mixed. This can sometimes be accomplished by putting a compatibilizer in the blend, or by causing a reaction to occur between the polymers in the blend, or sometimes by physical mixing.

Liquid crystalline polymers (LCP) and poly(phenylene oxide) polymers (PPO) individually have certain superior properties, but LCPs are relatively expensive, while PPOs cannot be readily processed (formed into shapes). Blends of these two polymers were thought to be potentially advantageous, but in order to obtain blends with good properties it has generally been found necessary to use a compatibilizer, and/or more commonly, to use a PPO containing added functionality (there are presumably some functional end groups that normally occur in PPOs, but these are not what is meant by functionalized PPO herein) that can potentially react with a compatibilizer or directly with the LCP, thereby improving the properties of the blend produced.

Likewise, attempts have been made to compatibilize LCP/PPO blends by requiring acid or ester functionality on the LCP to react with a hydroxyl or thio group on a PPO under catalytic conditions to form an ester or thioester. See for example, U.S. Patent 5,182,334. Of course, this necessarily limits the LCPs available since they all do not contain reactive acid or ester functionality. In either case, these methods add cost to the blend, and may adversely affect other properties. Therefore improved methods of producing LCP/PPO blends with good properties, as well as the improved blends themselves are desired.

U.S. Patent 5,498,689 and Japanese Patent Application 04/202461 describe the use of certain functionalized PPOs in blends with LCPs. None of

these references describes an LCP/unfunctionalized PPO which is said to have good physical properties or one which is not covalently linked by esterification.

European patent Application 438,128 A2 describes a method for making blends of an LCP with a non-LCP polymer. The PPOs used are functionalized PPOs which react with a bisoxazoline modifier.

Summary of the Invention

This invention concerns a polymer blend, comprising, about 5 to about 99 percent by weight of one or more thermotropic liquid crystalline polymers, and about 95 to about 1 percent by weight of an unfunctionalized poly(phenylene oxide), the percent by weight being based on the total amount of said liquid crystalline polymers and said poly(phenylene oxide) present, and wherein:

a discontinuous phase has a volume weighted width average particle size of about 40 μm or less; or

a co-continuous morphology is present in which the distance from any point within a co-continuous domain to the nearest interface with another phase or another phase inclusion is about 20μ or less; or

if a discontinuous and a co-continuous phase are both present, said discontinuous phase has a volume weighted width average particle size of about 40 μm or less, and said co-continuous morphology said distance from any point within said co-continuous domain to said nearest interface with another phase or another phase inclusion is about 20μ or less.

This invention also concerns a process for making a polymer blend, comprising, melt mixing about 5 to about 99 percent by weight of one or more thermotropic liquid crystalline polymers with about 95 to about 1 weight percent of an unfunctionalized poly(phenylene oxide), wherein percent by weight is based on the total amount of said liquid crystalline polymers and poly(phenylene oxide) present, at a sufficiently high shear and for a sufficient amount of time to produce a blend wherein:

a discontinuous phase is present and has a volume weighted width average particle size of about 40 μm or less;

a co-continuous morphology is present in which the distance from any point within a co-continuous domain to the nearest interface with another phase or another phase inclusion is about 20μ or less; or

said discontinuous and said co-continuous phase are both present, said discontinuous phase has a volume weighted width average particle size of about 40 μm or less, and said co-continuous morphology said distance from any point within said co-continuous domain to said nearest interface with another phase or another phase inclusion is about 20μ or less.

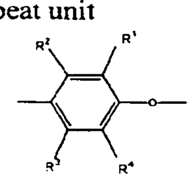
In addition to the invention described above, the invention also relates to blends of LCPs and functionalized PPOs wherein said blends have, in a discontinuous phase, a volume weighted width average particle size of about 40 μm or less; or in a co-continuous morphology, the distance from any point within a co-continuous domain to the nearest interface with another phase or another phase inclusion is about 20 μ or less, if both a discontinuous and a co-continuous phase are present, the volume weighted width average particle size is about 40 μm or less and the distances is 20 μ or less.

<u>Detailed Description</u>

A thermotropic liquid crystalline polymer herein is given it conventional meaning, is an LCP by the TOT test described in U.S. Patent 4,075,262, which is hereby included by reference. Any thermotropic LCP may be used in these compositions and processes. Suitable thermotropic LCPs. for example, are described in U.S. Patents 3.991,013, 3,991,014 4,011.199, 4.048,148, 4,075,262, 4.083,829, 4,118,372, 4.122,070, 4.130,545, 4,153,779, 4,159.365, 4,161,470, 4,169,933, 4,184,996, 4,189,549, 4,219,461, 4,232,143, 4,232,144, 4,245,082, 4,256,624, 4,269,965, 4,272,625, 4,370,466, 4,383,105, 4,447,592, 4,522,974, 4,617,369, 4,664,972, 4,684,712, 4,727,129, 4,727,131, 4,728,714, 4,749,769, 4,762,907, 4,778,927, 4,816,555, 4,849,499, 4,851,496, 4,851,497, 4,857,626, 4,864,013, 4,868,278, 4,882,410, 4,923,947, 4,999,416, 5,015,721, 5,015,722, 5,025,082, 5,086,158, 5,102,935, 5,110,896, and 5,143,956, and European Patent Application 356,226. Useful thermotropic LCPs include polyesters, poly(ester-amides), poly(ester-imides), and polyazomethines. Preferred thermotropic LCPs are polyesters or poly(ester-amides), and it is especially preferred that the polyester or poly(ester-amide) is partly or fully aromatic.

In a preferred embodiment and with unfunctionalized PPOs, the LCP(s) should have a viscosity of at least 20 Pa*s when measured at 1000 1/s shear rate at a temperature ≥ 330°C or at a higher temperature if the LCP will not flow at 330°C.

By an unfunctionalized poly(phenylene oxide) is meant (as known to those skilled in the art, see for instance U.S. Patent 5,212,255, which is hereby included by reference) a polymer with the repeat unit



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each of R^1, R^2, R^3 and R^4 are hydrogen or hydrocarbyl containing to 6 carbon atoms. In a preferred (I) herein R^1 and R^4 are methyl and R^2 and R^3 are hydrogen. The unfunctionalized PPO does not have any added functional groups present (i.e., is unfunctionalized), but "normally present" end groups may be present. Lower viscosity PPOs for easier mixing are preferred. Low molecular weight PPOs are also preferred.

The "functionalized PPOs" utilized herein can include those unfunctionalized PPOs having additional functional groups such as amines, anhydrides, or thioesters, epoxides, etc.

The blends described herein may exhibit several different morphologies, these morphologies being dependent on the relative amounts of LCP and PPO in the blend, and/or the shear history of the blend. If the majority by volume of the polymer is the LCP, is likely the LCP will be a continuous phase and the PPO a discontinuous phase, while if the majority by volume of the polymer is PPO, it is likely the PPO will be a continuous phase and the LCP will be a discontinuous phase. At about equal volumes of each polymer the morphology is less predictable, and co-continuous phases of LCP and PPO are more likely. Herein percent by weight of polymers in the blends is based on the total amount of polymer in the blend. One preferred blend contains about 5 to about 20 weight percent of LCP and about 95 to about 80 weight percent PPO. Another preferred blend contains about 50 to about 99 weight percent LCP, more preferably about 60 to about 75 weight percent LCP, and a complimentary amount of PPO.

By a continuous phase is meant that most or all of that polymer present in the blend is physically in contact will all of the other polymer of that type in the blend. If one were to somehow remove the second polymer without otherwise disturbing the blend, the polymer in the continuous phase would appear to be (almost) a single piece of polymer containing voids. By a discontinuous phase is meant that polymer is present in many discrete particles within the blend. The particles may include spheres, ellipsoids, and fibrils. Discontinuous PPO can be spherical or ellipsoidal in the center of molded 0.32 cm (0.125 in.) thick ASTM tensile bars microtomed perpendicular to the flow as described in the text below. In some cases such as Example 23, spherical or ellipsoidal PPO domains are present in the bar center and oriented PPO domains appear nearer the bar surface. For instance, elongated ribbon like PPO domains with length to diameter ratios of around 10:1 or more were present near the surface of the molding with progressively less orientation towards the bar center. These oriented domains are actually sheets (as evidenced by examination in the same region but microtomed parallel to the major axis of the tensile bar). The oriented region with sheets of

PPO in this particular example was about 0.64 mm (0.025 in.) thick projecting inward from and perpendicular to the surface of the 0.32 cm (0.125 in.) thick ASTM tensile bar used to characterize morphology. Discontinuous LCPs have more of a tendency (than PPOs) to be fibrils.

By a co-continuous morphology is meant that both polymers are present in continuous phases (i.e., "one piece") or at least substantial amounts of each polymer are physically attached to one another.

In these blends at least one of the LCP or PPO has a volume weighted width average particle size (VWPS) of about 40 μm or less, preferably about 15 μm or less. The VWPS is measured as described below. If there is some question as to whether the morphology may change in the final forming (such as molding) of a part, a suitable mold shall be placed on the same machine on which the final useful part is molded, and the prescribed VWPS test pieces molded. Blends which have the VWPS described herein tend to have relatively good physical properties, even in the absence of functionality on the PPO, and even in the absence of separate compatibilizers.

In blends (or the process for making them) where a co-continuous morphology is present it is preferred that the distance from any point within a co-continuous domain to the nearest interface with another phase or another phase inclusion is about 10μ or less.

Even though no functionality is present in the preferred PPO, and no compatibilizers may have been added, these blends can surprisingly be produced by simply melt mixing under certain conditions. These conditions are mixing under sufficiently high shear rates for a sufficient amount of time to produce a blend with the desired VWPS. Specific mixing conditions for any given blend can't be given, since this will depend on the LCP and PPO chosen, their molecular weights and molecular weight distributions (principally because these affect melt viscosity), the temperature at which the mixing is carried out, and other factors. However the following guidance can be offered to achieve the desired blend.

The two most important factors in achieving the desired blends are relatively high shear mixing (sometimes also called intensive dispersive mixing) of the components and viscosity matching of the LCP and PPO components of the blends. High shear mixing is known in the art, see for instance W. Thiele, Plastics Formulating & Compounding, vol. 2 (1996), p. 14-19. Although not necessary, such mixing may be conveniently carried out a twin-screw extruder equipped with the proper combination of mixing elements. Such elements and their combination are known in the art (see for instance Thiele), and are also described herein in the Examples.

By viscosity matching or "viscosity matched" is meant that at least for some part of the process where melt mixing and dispersion of the polymers may take place, the LCP and PPO have approximately the same effective (melt) viscosity. This can be achieved for instance by using one or more of the following methods:

The molecular weights and/or the molecular weight distributions of the LCP and/or PPO are adjusted so that they exhibit comparable melt viscosities in some part of the mixing process. This often may mean raising the LCP molecular weight and/or lowering the PPO molecular weight, since the more common grades of LCP tend to have lower viscosities than the common grades of PPO.

Another approach is to choose an LCP with a melting point between about 300–350°C. This corresponds to the temperature range where PPO becomes substantially melt processible. Substantially melt processible means the PPO viscosity is less than about 400 Pa*s at 1000 1/s. The LCPs with melt points between about 300°C–350°C may form higher performance blends with PPO more easily than lower melting LCPs. It is hypothesized that the PPO may soften first, before the LCP melts. As the LCP begins to melt the chance for phase inversion occurs which should tend to maximize interfacial area. It is hypothesized to be advantageous to operate the melt compounding process such that this maxima in interfacial area occurs(which should also coincide with transient viscosity matching) whilst subjecting the blend to a relatively high level of dispersive mixing.

For LCPs melting below about 300°C the compounding process may be run so that the solid state mixture of the feed ingredients is subjected to relatively high shear dispersive mixing before the LCP melted. In this way, the LCP melting transition coincides more closely with high shear dispersive mixing with the PPO.

Another approach that is useful is to add the low melting but unmelted LCP to a preheated PPO or substantially molten PPO in a way that the mixture rapidly encounters relatively high shear dispersive mixing before the LCP melts.

In the desired blends where there is an LCP continuous phase, useful combinations of properties approaching and in some cases surpassing those of commercially available unblended LCP products can be achieved, even when the blends are not compounded with common fillers such as glass fibers, minerals, talc, etc. This is generally not true for the base LCP from which the blends are made. Commercially useful, filled LCP products tend to have relatively high specific gravities of around 1.6 g/ml or higher which leads to heavy parts. On the other hand, the LCP/PPO blends of the current invention often have very useful

properties even without fillers and often exhibit superior surface qualities, high physical properties, a useful degree of flame resistance, and specific gravities as low as about 1.1 g/ml. Addition of fillers to the blends often offers other combinations of properties at reduced weight and cost versus comparable commercial LCP molding products.

Injection molding of the LCP/PPO blends is also an area where the blends often appear to be superior in comparison with commercially available LCP molding grades. The blends tend to process very smoothly, especially in injection molding screw retraction times and molding cycle screw retraction stability.

PPO continuous phase blends usually have useful combinations of physical properties, high temperature resistance and processability that are often unique versus existing PPO type products. For instance their melt viscosities are quite low, often in the range of 50-150 Pa*s.

Additives that are normally added to polymers may also be added to the LCP/PPO blends described herein. Such additives includes fillers, reinforcing agents, pigments, dyes, antioxidants, lubricants, flame retardants, and the like. Preferred fillers and/or reinforcing agents include talc, glass flake, glass fiber, carbon fiber, aramid fiber, carbon black, TiO_2, and the like. Compatibilizers for the LCP/PPO blend may also be added, and a preferred compatibilizer is a copolymer of an olefin such as ethylene with a copolymerizable monomer containing an epoxy group such as glycidyl (meth)acrylate. Repeat units derived from other monomers, such as (meth)acrylate esters may also be present in such copolymers. If a compatibilizer is present, a preferred range is about 0.5 to about 15 weight percent of the LCP/PPO blend present. A preferred compatibilizer copolymer contains ethylene, glycidyl acrylate or methacrylate, and optionally one or more acrylate or methacrylate esters. The most preferred compatibilizer is EBAGMA, a copolymer of ethylene, butyl acrylate and glycidyl methacrylate.

The LCP/PPO blends optionally containing epoxy functionalized acrylate ester copolymers or epoxy functionalized polyolefins often have even better surface appearance than the LCP/PPO blends without compatibilizer. In addition, blends containing compatibilizers such as epoxy functionalized acrylate ester copolymers or epoxy functionalized polyolefins tend to have somewhat higher tensile elongation than blends without compatibilizers. The higher elongation indicates that these materials are somewhat tougher than the LCP/PPO blends without compatibilizers. Surprisingly, many of these blends are flame resistant, having a rating of V-0 at 1/16" (1.6 mm) thickness when tested using the Underwriter's Laboratories UL-94 test, even though they contain highly flammable ingredients such as epoxy functionalized acrylate ester copolymers or

epoxy functionalized polyolefins. Also, the epoxy modified blends often have significantly more complex morphologies, such as particles within particles and more integrity to the interfaces between the major PPO/LCP phases.

The epoxy containing polymer is preferably a functionalized ethylene copolymer E/X/Y with 45-99 weight percent E (ethylene), 0-40 weight percent X which is one or more softening monomers chosen from C_1-C_{10} esters of acrylic and/or methacrylic acids or vinyl esters, and 1-15 weight percent Y which is a co-monomer chosen from glycidyl acrylate, glycidyl methacrylate and glycidyl vinyl ether.

Particle Size Analysis Method

The compositions of the invention were injection molded according to the procedure given below into ASTM D 638 Type 1 Tensile bars with 3.18 mm (0.125 in.) thickness and overall length of 21.9 cm (8.625 in.). The injection gate is on the edge of the bar at about 3.2 cm (1.25 in.) along the major axis from one end of the tensile bar hereafter identified as the near end. The gate dimensions were approximately 6.4 mm (0.25 in.) in length by about 2.54 mm (0.100 in.) thick with the gate being flush with the bar surface opposite the knock out pins. The tensile bar was cut or sectioned about 2.5 cm (1 in.) from the far end (the other end without the injection gate) across the bar or transverse to the flow direction (i.e. perpendicular to the major axis of the bar). This cut is made in the wider portion of the tensile bar [1.9 cm. (0.75 inch) wide]. The sectioning was performed cryogenically at liquid nitrogen temperature using a Leica® SM2500E microtome equipped with a stainless steel knife. Section thickness was about 8–10 μm. Particle size analysis was conducted on sections obtained not closer than 0.64 mm (0.025 in.) from the original surface of the bar. Another way to describe this is to consider a hypothetically perfect 8–10 μm section cut as just described with dimensions of approximately 8–10 μm by 3.18 mm (0.125 in.) by 1.9 cm (0.75 in.). The 8–10 μm thick edge would be cut off at least 0.64 mm (0.025 in.) around this rectangular box leaving a new box with dimensions of 8–10 μm by about 1.9 mm (0.075 in.) by about 1.8 cm) (0.70 in.). This inner section with no surfaces from the original molding was then examined microscopically.

The sections obtained were affixed between glass slides and coverslips using Canada balsam and photographed using phase contrast bright field and polarized light illumination on a Leitz® optical microscope. Magnifications of either 50x or 100x were then used for image analysis of compositions of the invention described in Table 4.

Transmission Electron Microscopy must be used to generate images for the preferred compositions below about 15 μm (having significantly finer particle

size distributions than those described in Table 4). The same protocol is used to microtome these preferred, more finely dispersed samples. The preferred compositions can have particulate or co-continuous morphologies or co-existence of particulate and co-continuous morphologies. These various morphologies of the preferred compositions are made even more complex by the existence of phases within phases and are not readily describable by image analysis. The compositions will have less than or equal to an number average of 20 μm linear distance from any point within a co-continuous domain or particulate domain to the nearest interface with the other phase (which could be an included domain). The preferred compositions have about 10 μm or less number average linear distance from any point within a co-continuous domain or particulate domain to the nearest interface with the other phase (which could be an included domain).

Particle size was determined using a Cambridge Instruments Quantimet® 970 image analysis system. The photographed images generated by optical microscopy or T.E.M. are then digitized using a high resolution video camera. The field size used was typically 800x625 pixels. The system was normally calibrated using an image of the calibration scale or by the scale marker located directly on the optical micrographs. This image is then segmented to form a binary (on-off) image of the features of interest. The image is subsequently analyzed using a program which yields the various dimensional parameters of interest. This program is readily understood by an artisan skilled in image analysis. A good source of information about image analysis can be found in the book: "Practical Stereology" by John C. Russ. Plenum Press. NY, 1986. The output of the analysis used in this work consists of distributions of the number weighted length (particles largest dimension), breadth (particles short dimension, calculated by dividing the particle area. which is generated by Quantimet® 970 image analyzer, and dividing by length), and equivalent circular diameter (the diameter of a circle occupying the same area as the particle). The program also calculates the volume weighted distributions of these same parameters by assuming that the particle is an ellipsoid of revolution about the major axis. The output is displayed both as a histogram as well as cumulative bar chart. The mean and standard deviations of the distributions are also determined and are reported in Table 4 for compositions of the invention.

EXAMPLES

In the Examples certain materials are used. They are summarized below:

PPO The PPOs used were obtained from the General Electric Co., Stamford, CN. U.S.A., and a description of such polymers can be found in U.S. Patent 5,212,255 which is incorporated by reference. PPO-4 has an inherent

viscosity of about 0.4. and PPO-3 had an inherent viscosity of about 0.3. Melt viscosities are shown in Table 1.

LCPs (all in mole percent): The viscosities of the LCPs are shown in Table 1.

LCP 1: 20% hydroquinone. 6.5% terephthalic acid, 7% isophthalic acid, 6.5% 2,6-napthalenedicarboxylic acid, 60% 4-hydroxybenzoic acid, with a melting point of about 330°C. Several different samples with varying viscosity were made.

LCP 2: 10% Hydroquinone, 10% 4,4'-biphenol. 14% terephthalic acid, 6% 2,6-napthalenedicarboxylic acid. and 62% 4-hydroxybenzoic acid. It had a melting point of about 340°C.

LCP 3: 21% Hydroquinone, 11% isophthalic acid, 11% 2,6-napthalenedicarboxylic acid, and 57% 4-hydroxybenzoic acid. It had a melting point of about 270°C.

Table 1

Melt Viscosities in Pa*s at 1000 1/s

Temp. °C	LCP				PPO	
	1	1H	2	3	PPO-3	PPO-4
325				77	366	550
350	66	220	60	60	70	273

Compatibilizers

Compatibilizer 1 ("EBAGMA"): This polymer was made under high pressure conditions was 66.3 weight percent ethylene. 28.5 weight percent butyl acrylate and 5.2 weight percent glycidyl methacrylate and had a melt index of 12 (2160 g weight, 190°C).

Compatibilizer 2: A polyethylene made by high pressure polymerization containing 4-4.5 mole percent copolymerized glycidyl methacrylate. It had a melt index of 35.8 (2160 g weight, 190°C).

Other Ingredients

Glass 1 - Chopped glass fiber available as OCF464AA from Owens Corning Fiberglass Co. Toledo. OH, USA.

Glass 2 - Chopped glass fiber available as PPG3563 from PPG Industries, Pittsburgh, PA, USA.

Flame retardant 1 (FR-1) - REOFOS RDP, an oligomeric organic phosphate available from FMC Corp. (UK) Limited, Process Additives Div., Tenax Rd.. Trafford Park. Manchester M17 1WT, United Kingdom.

Talc 1 - Polytal® 4545 from Whittaker. Clark & Daniels, Inc.

Test Methods

Tensile strength and elongation was measured on 3.2 mm (1/8") thick tensile bars with a crosshead speed of 0.51 cm (0.2")/min according to ASTM D638-91. Strain gauges were used to accurately determine elongation.

Flexural modulus was measured on 1.6 mm (1/16") thick flexural bars according to ASTM D790-92.

Heat resistance at 250°C was qualitatively measured as follows. A 1.6 mm (1/16") thick flex bar held vertically by a clamp was completely immersed in a 250°C molten metal bath and help stationary for 60 s. The high density of the molten metal naturally tends to force the submersed lower density flex bar towards the surface. If the bar has significant modulus at this temperature it would not be deflected or curled from planar whereas if the modulus was too low, the bar would curl to a significant extent. In addition any undesirable surface bubbling or blistering would be noted. This test provides some qualitative indication of how well a given material might perform under conditions used for IR soldering of electronic connectors and other electronic components. A rating of 0,nb means the sample had zero distortion from planarity (0) caused by the heat and load of the molten metal bath and did not blister (nb or no blistering).

Heat distortion temperature was measured on some samples according to ASTM D648 at 1.8 MPa.

Melt viscosity or MV was determined on a Kayeness rheometer (Kayness, Inc., RD #3, Box 30, E. main St., Honeybrook, PA 19344 U.S.A.) with a die hole size 0.05 mm (0.02") diameter by 2.0 cm (0.08") long using a 300 s premelt time. The temperature was 350°C unless otherwise noted. Samples were dried for at least 3 h at 120°C before measuring MV. Melt viscosities were measured at 350°C unless otherwise noted.

Surface appearance was judged visually by noting flow lines, surface smoothness or other irregularities in the surface of molded test bars. The blends tended to have superior surface properties compared with the base LCP's from which the blends were produced.

Flammability was determined according Underwriters Laboratory Test UL-94 on 1.6 mm (1/16") thick flex bars.

Blend And Test Part Preparation

The blends were prepared using a 30mm Werner & Pfleiderer Model 10YHD (Werner & Pfleiderer, 663 E. Crescent, Ramsey, NJ 07446 U.S.A.) twin screw extruder with LCP's dried at about 110°C-120°C in a nitrogen purged vacuum oven for about 12 h (or overnight). The screw design is shown in Table 2.

The symbols used for the bushings are those used by Werner and Pfleiderer. The extruder was operated at 250 rpm with feed rates of about 11.3 kg (25 lb)/h. Temperature profiles for the 4 heating zones of the machine for the LCP-1 and LCP-2 blends were about 290°C (barrel 1); 320°C (barrel 2); 310-320°C (barrels 3 and 4) and 335°C for the die. The temperature profile for the LCP-3 blends was 260°C (barrel 1); 290°C (barrel 2); 290°C (barrels 3 and 4) and 335°C on the die. A 3.2 mm (1/8") or 4.8 mm (3/16") dia. one hole die was used. The extrusion screw design and conditions utilized are typical of the type used. The extruded strands were quenched in a water trough cooling bath. cut into pellets, dried at 120°C overnight and subsequently injection molded into test bars.

Table 2

Element No.	Bushing Type	Comments	Number of Bushings	Cumulative Length (mm)
1	PD		1	10
2	42/42 R	SK_Feed	2	94
3	42/21 R	SK_Ramp	1	115
4	28/28 R		3	199
5	KB 28 R		1	227
6	KB 42 N		1	269
7	KB 14 N		1	283
8	20/10 L		1	293
9	42/42 R		2	377
10	28/28 R		1	405
11	20/10 L		1	415
12	42/42 R		2	499
13	KB 20 R		2	539
14	KB 28 N		1	567
15	20/10 L		1	577
16	42/42 R	SK_FEED (vacuum port)	3	703
17	42/42 R		1	745
18	20/10 L		1	755
19	28/28 R		2	811
20	KB 14 N		1	825
21	20/20 R		1	845
22	14/14 R		3	877

Dried blend pellets prepared above were injection molded on a 171 g (6 oz) HPM injection molding machine (HPM Corp. 200-TP 6.5-6.5 6 z. Injection Molding Machine, HPM Corp., 820 Marion Rd., Gilead, OH 43338, U.S.A.) equipped with a general purpose type screw. The LCP-3 blends were molded with the barrel temperatures at: 280°C (rear); 285°C (center); 285°C (front); 285°C (nozzle). The LCP-1 blends were molded with barrel temperatures of: 330°C (rear); 330°C (center); 330°C (front); 330°C (nozzle) while the LCP-2 blends were processed with barrel temperatures of 340°C (rear); 335°C (center); 335°C (front); 335°C (nozzle). Mold temperature was 100°C. Molding cycle

(boost/injection/hold) was 3/20/20 s with screw at 120 rpm, fast ram speed and minimal back pressure. The blends processed very easily and generally had superior screw retraction times and stability compared with the corresponding unblended LCPs. The mold used had three cavities: 2.54 cm x 3.2 mm (1x0.125") thick tensile bar (ASTM D638-91); 2.54 cm x 3.2 mm (1x0.125") thick flexural (flex) bar (ASTM D790-92); and 2.54 cm x 1.6 mm (1x0.0625") thick flex bar.

Examples 1-12 and Comparative Examples A and B

Table 3 lists these Examples and the results obtained. Beneath each ingredient the weight fraction of that ingredient is given.

The blend of Example 1 had a density of 1.24 g/ml.

The "LCP-1H" of Example 2 means this polymer which was further solid state polymerized had a viscosity of 200 Pa*s.

The blend of Example 4 had a very low melt viscosity of 23 Pa*s and surprisingly did not drip during UL-94 flammability testing.

Examples 13*-22

The weight fraction of each ingredient is again shown below that ingredient in Table 4. Example 13* is the comparative example for the filled blends in Table 4.

Examples 23-24 and Comparative Example

These are shown in Table 5. In each case the LCP was LCP-1 in a weight fraction of 0.65, combined with PPO-4 in a weight fraction of 0.35. The viscosities of the LCP-1 were varied and are shown in Table 5. These examples relative to the comparative example clearly demonstrate that particle sizes as claimed (about 40μm or less) provide significant advantages (e.g., tensile strength) over the blends having larger particle sizes as shown in Table 5. In these examples, varying the viscosity of the LCP following the blend preparation procedure described herein resulted in a comparative example (with particle sizes outside Applicant's range) and examples 23-24 (within range).

Table 3

Example	LCP	PPO	OTHER	Ten. Str. MPa	Ten. Elong. %	Flex. Mod. GPa	Heat Resistance	MV(Pa*s) 1000 1/s	SURFACE	UL-94 1/16"
A	1 1			167	1.5	14	0,n	66	poor	V-0
B	2 1			149	1.6	11	0,n	60	poor	V-0
1	1 0.686	PPO-4 0.243	EBAGMA 0.071	124	2.6	8.3	---	85	excellent	V-0
2	1H 0.686	PPO-4 0.243	EBAGMA 0.071	161	2.3	9.0	---	127	excellent	V-0
3	2 0.68	PPO-4 0.26	EBAGMA 0.06	106	4.0	5.5	0,nb		excellent	V-0
4	2 0.68	PPO-4 0.32	---	108	2.4	7.6	0,nb	23	good	V-0
5	3 0.686	PPO-4 0.243	EBAGMA 0.071	88.9	2.6	6.9	---	---	excellent	V-0
6	1 0.589	PPO-4 0.35	EBAGMA 0.061	98.6	2.7	6.9	---	70	excellent	V-0
7	1 0.589	PPO-4 0.318	EBAGMA 0.093	118	2.9	6.2	---	87	excellent	V-0
8	1 0.48	PPO-4 0.402	EBAGMA 0.118	73.8	2.6	4.1	---	100	excellent	V-1
9	1 0.48	PPO-3 0.52	---	114	1.9	7.6	---	100	excellent	
10	1 0.45	PPO-3 0.49	EBAGMA 0.06	101	2.1	4.7	---	100	excellent	
11	1 0.3	PPO-3 0.64	EBAGMA 0.06	91.7	2.8	3.6	---	100	excellent	
12	1 0.1	PPO-3 0.9		75.1	4	3.3	HDT 174°C	55	good	

Table 4

EX.	LCP	PPO	OTHER POLYMER	Filler	Filler	Other	Ten. Str. MPa	Ten. Elong. %	Flex. Mod. GPa	Heat Resis.	MV(Pa*s) 1000 1/s	SURFACE	UL-94 1/16"
13*	L330 0.7			Glass1 0.3			145	1.5	13.8	0,n	60	good	V-0
14	L330 0.48	PPO-4 0.17	EBAGMA 0.05	Glass1 0.3			86.2	1.5	11.7		70	good	
15	L330 0.48	PPO-4 0.17	EGMA 0.05	Glass1 0.3			86.9	1.2	11.7		80	good	
16	L340 0.58	PPO-4 0.18	EBAGMA 0.04	Glass2 0.2			97.9	2.5	7.58	0,n		good	V-0
17	L330 0.55	PPO-4 0.25			Talc 0.2		110	1.7	11.0		43	good	V-0
18	L330 0.48	PPO-4 0.18	EBAGMA 0.04	Glass2 0.1	Talc 0.2		95.1	1.6	8.34		80	good	V-1
19	L330 0.47	PPO-4 0.17	EBAGMA 0.04	Glass2 0.1	Talc 0.2	RDP 0.02	103	1.6	8.69		79	good	V-0
20	L330 0.1	PPO-3 0.6		Glass2 0.1	Talc 0.2		88.2	2.1	7.03		79	good	V-1
21	L330 0.1	PPO-3 0.55		Glass2 0.1	Talc 0.2	RDP 0.05	94.4	2.1	6.83		61	good	V-0
22	L330 0.075	P3 0.675		Glass1 0.25			148	2.4	8.27	HDT 200C	112	exc.	

13* is comparative example

Table 5

						Average Particle Size[a]						
	LCP	Ten. Str.	Elong.	Flex. Mod.		Number Average			Volume Weighted[c]			Total
EX.	Visc.	MPa	%	GPa	[b]	L	W	D	L	Wd	D	Count
23	61 Pa-s	121	1.8	11.3	x	34.0	13.2	23.8	55.2	20.3	37.6	371
					s	18.0	5.7	10.8	20.1	6.3	12.0	
24	27 Pa-s	85.5	1.5	9.38	x	38.6	18.5	29.9	98.3	38.5	68.7	286
					s	31.9	12.6	21.8	56.0	12.4	29.9	
Comp	10Pa-s	44.8	1.1	8.69	x	124	40.9	79.0	846	277	543	649
					s	182	54.6	109	335	120	218	

[a] Particle sizes using Quantimet®-970 Image Analyzer.
[b] Mean (x), standard deviation (s), length (l), width (w), equivalent circular diameter (D), all in μm.

[c] Volume weighted averages calculated using the formula $V = 3.14LW*W/6$.
Wd is volume weighted width average particle size

These non-limiting examples demonstrate that the blends of the invention have good physical properties for the uses specified herein relative to non-blended LCPs. The specific mixing conditions described for preparation of examples 1-24 are included within the conditions generally specified as "sufficiently high shear" for a "sufficient amount of time." The specific ratios of LCP to PPO for the specific polymers listed in the examples are equally applicable to any LCP/PPO blend as generally described herein provided that the appropriate mixing conditions are utilized to effect a volume weighted width average particle size of less than about 40 μm in a discontinuous phase or, in a co-continuous morphology, the distance from any point within a co-continuous domain to the nearest interface with another phase or another phase inclusion is about 20μm or less in said blends. One of ordinary skill in the art with the guidance provided herein can vary the specific equipment described, temperatures, times, etc. and match or approximately match the viscosities of the individual liquid crystal polymer and individual PPO to form blends having the particle sizes and/or distances referred to herein.

The present invention further includes blends made from the processes described herein and includes articles prepared from said polymeric blends or articles having said blends as a component or constituent therein including solderable electronic components.

CLAIMS

What is claimed is:

1. A polymer blend, comprising

(a) about 5 to about 99 weight percent based upon the combined weight of (a) and (b) of at least one thermotropic liquid crystalline polymer; and

(b) about 95 to about 1 weight percent of an unfunctionalized poly(phenylene oxide)

wherein, at least one of the blend components (a) or (b) has a volume weighted width average particle size (VWPS) of about 40μm or less or, in a blend having a co-continuous domain, the distance from any point within the co-continuous domain to the nearest interface with an adjacent phase or phase inclusion is about ≤20 μ.

2. A polymer blend, comprising, about 5 to about 99 percent by weight of one or more thermotropic liquid crystalline polymers having a viscosity of at least 20 Pa*s when measured at 1000 1/s shear rate at a temperature of ≥ 330°C or at a higher temperature if the LCP will not flow at 330°C, and about 95 to about 1 percent by weight of an unfunctionalized poly(phenylene oxide), the percent by weight being based on the total amount of said liquid crystalline polymers and said poly(phenylene oxide) present. and wherein:

a discontinuous phase has a volume weighted width average particle size of about 40 μm or less; or

a co-continuous morphology is present in which the distance from any point within a co-continuous domain to the nearest interface with another phase or another phase inclusion is about 20μ or less; or

if a discontinuous and a co-continuous phase are both present, said discontinuous phase has a volume weighted width average particle size of about 40 μm or less, and said co-continuous morphology said distance from any point within said co-continuous domain to said nearest interface with another phase or another phase inclusion is about 20μ or less.

3. The polymer blend as recited in claim 1 wherein a discontinuous phase is present.

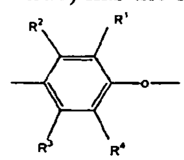
4. The polymer blend as recited in claim 3 wherein said volume weighted width average particle size is about 15 μm or less.

5. The polymer blend as recited in claim 1 wherein said blend is about 50 to about 99 percent by weight of said thermotropic liquid crystalline polymer.

6. The polymer blend as recited in claim 1 wherein said blend is about 60 to about 75 percent by weight of said thermotropic liquid crystalline polymer.

7. The polymer blend as recited in claim 1 wherein said thermotropic liquid crystalline polymer is a polyester or a poly(ester-amide).

8. The polymer blend as recited in claim 1, 2, 3, 4, 6 or 7 wherein said unfunctionalized poly(phenylene oxide) has the formula



(I)

wherein R^1 and R^4 are methyl and R^2 and R^3 are hydrogen.

9. A process for making a polymer blend, comprising, melt mixing about 5 to about 99 percent by weight of one or more thermotropic liquid crystalline polymers with about 95 to about 1 weight percent of an unfunctionalized poly(phenylene oxide), wherein percent by weight is based on the total amount of said liquid crystalline polymers and poly(phenylene oxide) present, at a sufficiently high shear and for a sufficient amount of time to produce a blend wherein:

a discontinuous phase is present and has a volume weighted width average particle size of about 40 μm or less:

a co-continuous morphology is present in which the distance from any point within a co-continuous domain to the nearest interface with another phase or another phase inclusion is about 20μ or less; or

said discontinuous and said co-continuous phase are both present, said discontinuous phase has a volume weighted width average particle size of about 40 μm or less, and said co-continuous morphology said distance from any point within said co-continuous domain to said nearest interface with another phase or another phase inclusion is about 20μ or less.

10. The process as recited in claim 9 wherein a discontinuous phase is present.

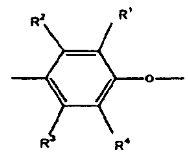
11. The process as recited in claim 10 wherein said volume weighted width average particle size is about 15 μm or less.

12. The process as recited in claim 9 wherein said blend is about 50 to about 99 percent by weight of said thermotropic liquid crystalline polymer.

13. The process as recited in claim 9 wherein said blend is about 60 to about 75 percent by weight of said thermotropic liquid crystalline polymer.

14. The process as recited in claim 9 wherein said thermotropic liquid crystalline polymer is a polyester or a poly(ester-amide).

15. The process as recited in claim 9, 10, 11, 13 or 15 wherein said unfunctionalized poly(phenylene oxide) has the formula



(I)

wherein R^1 and R^4 are methyl and R^2 and R^3 are hydrogen.

16. The process as recited in claim 9 wherein said melt mixing is done in a twin screw extruder.

17. The process according to claim 9 wherein the thermotropic liquid crystalline polymer and the unfunctionalized poly(phenylene oxide) are viscosity matched.

18. The process according to claim 9 wherein the viscosity of the liquid crystalline polymer is at least 20 Pa*s when measured at 1000 1/s shear rate at a temperature of ≥ 330°C or at a higher temperature if the LCP will not flow at 330°C.

19. A polymer blend produced from the process according to claim 17.

20. The polymer blend as recited in claim 1 or 2 additionally comprising a functionalized ethylene copolymer E/X/Y containing 45-99 weight percent E,

ethylene, 0-40 weight percent X which is one or more softening monomers chosen from C_1-C_{10} esters of acrylic or methacrylic acid, and 1-15 weight percent Y which is a co-monomer chosen from the group consisting of glycidyl acrylate, glycidyl methacrylate and glycidyl vinyl ether.

21. The process as recited in claim 9 wherein comprising a functionalized ethylene copolymer E/X/Y containing 45-99 weight percent E, ethylene, 0-40 weight percent X which is one or more softening monomers chosen from C_1-C_{10} esters of acrylic or methacrylic acid or vinyl esters, and 1-15 weight percent Y which is a co-monomer chosen from the group consisting of glycidyl acrylate, glycidyl methacrylate and glycidyl vinyl ether is also present.

22. The polymer blend as recited in claim 1 wherein said co-continuous morphology is present and in which the distance from any point within a co-continuous domain to the nearest interface with another phase or another phase inclusion is about 10μ or less.

23. The process as recited in claim 9 wherein said co-continuous morphology is present in said blend and in which the distance from any point within a co-continuous domain to the nearest interface with another phase or another phase inclusion is about 10μ or less.

24. A molded article fabricated from a polymer blend according to claim 1 or 2.

25. A polymer blend, comprising

(a) about 5 to about 99 weight percent based upon the combined weight of (a) and (b) of at least one thermotropic liquid crystalline polymer; and

(b) about 95 to about 1 weight percent of a functionalized or unfunctionalized poly(phenylene oxide)

wherein, in a blend having a discontinuous phase, at least one of the blend components (a) or (b) has a volume weighted width average particle size (VWPS) of about 40 μm or less, or, in a blend having a co-continuous domain, the distance from any point within the co-continuous domain to the nearest interface with an adjacent phase or phase inclusion is about ≤ 20μ.